Options for enhancing the storage of carbon dioxide in the oceans

Baar, H.J.W. de

Published in:
Energy Conversion and Management

DOI:
10.1016/0196-8904(92)90066-6

Publication date:
1992

Energy Convers. Mgmt Vol. 33, No. 5–8, pp. 635–642, 1992
Printed in Great Britain

0196-8904/92 $5.00+0.00
Pergamon Press Ltd

OPTIONS FOR ENHANCING THE STORAGE OF CARBON DIOXIDE IN THE OCEANS: A REVIEW

H.J.W. De Baar

Netherlands Institute for Sea Research, P.O.Box 59, 1790 AB Den Burg, The Netherlands

ABSTRACT

The various proposed options for enhancing CO_2 storage are often ingenious but rarely feasible. Fertilizing the central gyres would require enormous amounts of N and P fertilizer. Addition of iron to the Southern Ocean has been rejected as inefficient. The deep sea disposal of 50-100% of fossil fuel CO_2 would suppress the predicted transient peak of atmospheric CO_2 but eventually the atmospheric CO_2 level will be the same as without, unless rapid buffering by dissolution of calcite is significant. Ocean disposal applies only to point sources representing ~30% of fossil fuel emissions; relocation of these plants to maritime regions may not be economical either. Also ocean disposal costs ~30-45% of the energy produced. Current research is focusing on production and oceanic mixing behaviour of the effluent stream (this volume). In this paper the fate of the disposed CO_2 is assessed. The various proposed forms appear chemically unstable relative to ambient seawater. However the higher CO_2 contents of seawater might lead to part of the CO_2 being buffered forever through enhanced dissolution of existing calcite deposits. The predicted impact depends on the selected rate constant of latter dissolution. Ocean dumping is a fallback option, in case the sensible options of energy conservation and shifting to other energy sources would not be implemented adequately. Latter options would require societal and economic adaptations but appear the most efficient, if not inevitable, policy for imminent reduction of CO_2 emissions.

INTRODUCTION

The low level of about 0.03 % carbon dioxide (CO_2) in our atmosphere has largely been achieved by the marine biota. Over hundreds of millions of years some $50x10^{18}$kg or 50 million Gigaton C (GtC) as limestone ($CaCO_3$) and another 12 million GtC organic matter has accumulated within deep sea sediments (Fig. 1). Another portion is stored in continental soils, partly also as fossilized coal. As a result the atmosphere contains only about 700 GtC which exchanges at a rate of ~40-100 GtC/y with the surface ocean. Over several geological time scales this small amount of CO_2 in the atmosphere has varied, often preceded by orbital forcing and closely followed (Shackleton and Pisias, 1985) by variations in global temperature (Barnola *et al.*, 1987; Berner, 1991).Mankind has burned increasing amounts of fossil fuels and the atmospheric CO_2 rapidly increased with ~2-3 GtC/y from about 0.028% (280 x 10-6 atm) in 1850 to about 0.036% today, very fast compared to the changes over geological time. The biosphere has lived through previous dramatic change events, but not without massive extinctions. Comparison with industrial production records has learned that only ~60% of the emissions remain in the atmosphere, the other ~40% apparently is taken up by the oceans (Goudriaan, 1990).

In temperate zone surface waters the CO_2-fixation by marine algae is limited severely by depletion of essential nutrients nitrogen (N) or phosphorus (P). In high latitude waters the productivity may be limited by a variety of other factors (Lancelot *et al.*, 1992): low ambient light, also due to ice cover and intense cloud cover; absence of iron (Fe) as required in minute amounts for algal growth; or intense grazing pressure keeping algal biomass hence productivity at minimal levels. The relative importance of and interaction between these various factors is not well understood. Nevertheless there is unanimous agreement that shifts of marine biological productivity, notably in (sub)polar waters, exert a major control on changes of atmospheric CO_2, hence climate (Broecker and Denton, 1989; Charles and Fairbanks, 1992).

The pathways for net transfer of CO_2 from the atmosphere into the deep ocean are several, all of them necessarily going through surface waters. These euphotic surface waters, where penetrating light is driving photosynthetic CO_2 fixation, are well separated from the deep waters by a strong thermal gradient (at ~200-600m depth) preventing vertical mixing between surface and deep ocean. Only in the polar regions sinking of cold waters occurs in the northern North Atlantic Ocean and the Antarctic Weddell Sea during the northern and austral winters respectively. The cold waters draw down quite some dissolved CO_2, as well as Dissolved Organic Carbon (DOC). In addition to these two pathways there is a worldwide raindown of

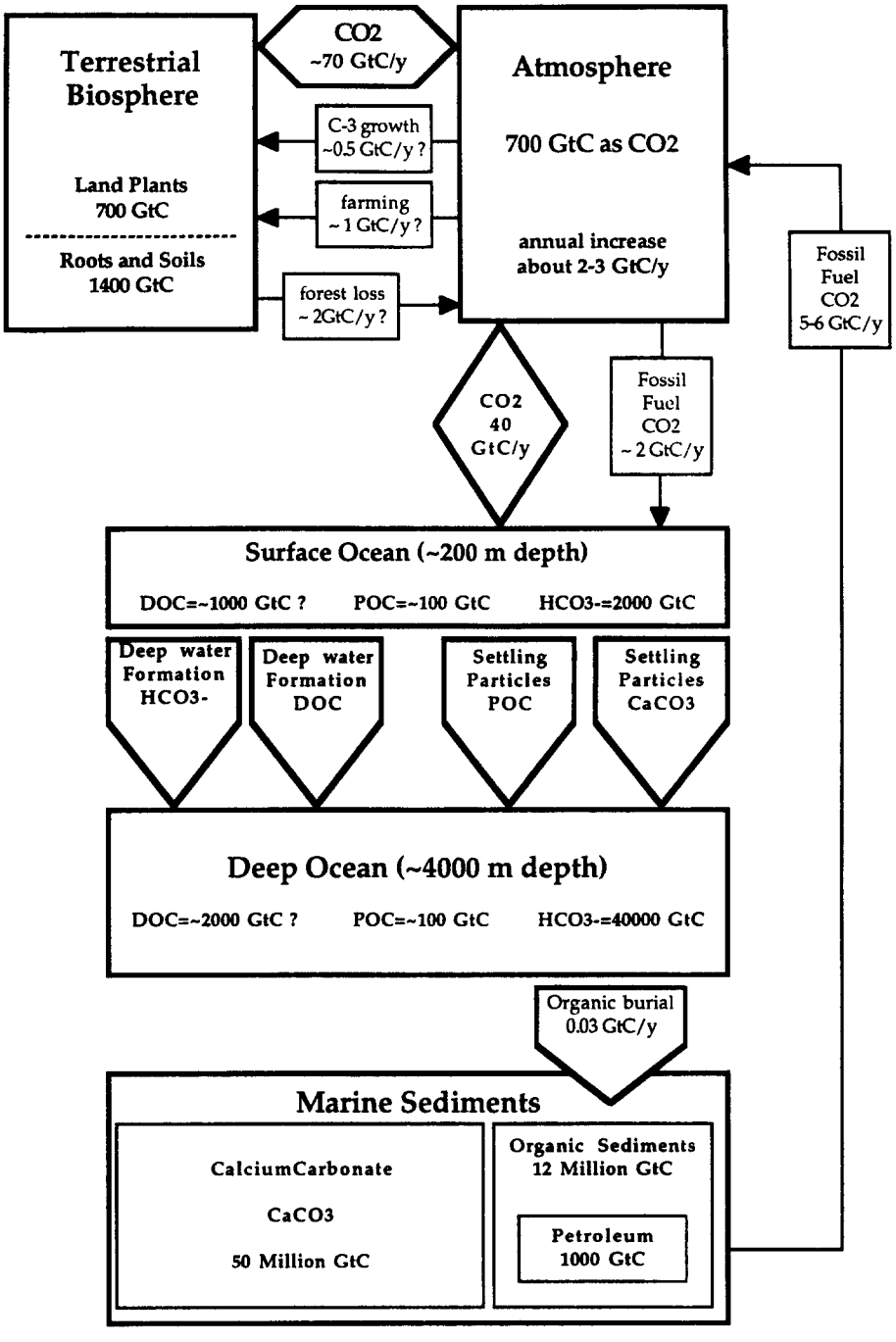

Fig. 1. The global carbon cycle with inventories in Gigaton C (1 GtC=10^{15} gram) and annual fluxes in GtC/y. Large bold arrows denote natural fluxes, small arrows fluxes caused by mankind. All values are approximations.

biological debris, settling particles containing both organic C as well as biogenic $CaCO_3$ tests. This export production is only a few percent of the gross photosynthetic C fixation which is mostly recycled again to CO_2 within the complex foodweb of the euphotic zone (De Baar and Stoll, 1989). Once in the deep ocean most of the exported particles are again mineralized to CO_2: consumed by bacteria, devoured by animals living on the seafloor, or slowly dissolving (the $CaCO_3$). However a very small percentage is buried into the sediments, eventually leading to the massive C reservoirs mentioned above.

Intentional enhancement of oceanic CO_2 uptake has been suggested to remedy the expected increase of atmospheric CO_2 by fossil fuel burning. One concern here is the implicitly assumed right to solve an environmental problem in one compartment of the biosphere by tinkering with yet another compartment.

Leaving aside this important matter for the moment one would allow oneself to examine the feasibility of schemes for enhancing oceanic CO_2 storage.The various schemes rely either on intentional fertilization or on bypassing both the atmosphere and the surface ocean by collecting fossil fuel CO_2 directly at its source and pumping it into the deep sea.

INTENTIONAL FERTILIZATION.

Macronutrients.

The addition of N and P to nutrient starved central gyres of the oceans in temperate zones would extend the current coastal eutrophication into the open ocean. Recently the possible effect of eutrophication in the North Sea on the atmospheric CO_2 budget was assessed. Despite major uncertainties it was deemed trivial: enhancement of gross photosynthesis is rapidly mineralized again i.e. no net increase of storage of C in the sediments (Hoppema and De Baar, 1991). The shallow NorthSea is very well mixed vertically, there is no deep water layer isolated from exchange with the atmosphere. On the other hand the central ocean surface waters are well separated from the underlying deep waters. Settling biogenic particles transport C down into the deep waters where they are mineralized again but the ensuing dissolved CO_2 is out of contact with the atmosphere. This biological pump already operates but might be enhanced. Marine algae take up C, N and P in fairly uniform proportions C:N:P=106:16:1 (Redfield *et al.*, 1963). For each additional 1 GtC/y to be fixed some 0.15 GtN/y and 0.01 GtP/y are needed. When N and P are recycled less efficiently than C in the surface ocean ecosystem they would be exported downward more rapidly; then the proportions of added N and P would have to be raised versus C to be removed. Clearly the amounts of N and P required would be enormous, as is the challenge of spreading this evenly over large and remote areas. The one initiative to work out such scheme apparently was abandoned (Broecker, 1977).

Fe fertilization.

In 1987 Fe enrichment experiments were done in the sub-Arctic North Pacific Ocean, where results hinted at possible Fe limitation (Martin and Fitzwater, 1988). Latter conclusion was challenged (Banse, 1990). On the other hand an independent experiment run simultaneously also supports the Fe limitation concept for this region (Coale, 1991). From this work in the subArctic it was extrapolated repeatedly that Fe would be the limiting factor for all of the Southern Ocean (Martin *et al.*, 1988; 1989; Martin, 1990), but direct evidence was lacking. Esoteric schemes for spreading Fe over all the Southern Ocean followed (Anonymous, 1990).

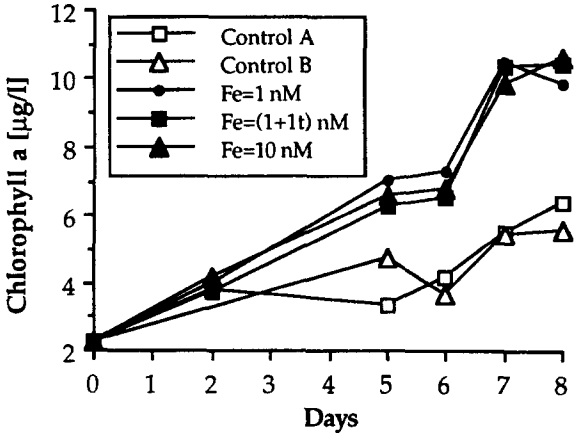

Fig. 2. Stimulation of phytoplankton growth (Chlorophyll a) upon addition of 1 nM, 1 nM + daily extra 1nM and 10nM Fe to seawater collected at 59°S, 49°W in the Weddell/Scotia Seas. Note that untreated controls also outgrow the initial field conditions (DeBaar et al., 1990).

The first Antarctic Fe enrichment experiments were executed in 1988 in the Weddell-Scotia Seas (De Baar *et al.*, 1989; 1990). Here Fe was found to stimulate biomass, however the untreated controls also outgrew the field (Fig. 2). Latter observation was ascribed to the exclusion of larger grazers from the experiments (Buma *et al.*, 1991), i.e. in the field the algal biomass would be kept low by intense grazing. In 1989 very similar results were obtained at 3 stations in the Ross Sea but this led to the opposite conclusion, i.e. Fe presumably being the major growth limiting factor (Martin *et al.*, 1990a). Latter conclusion was challenged by Dugdale and Wilkerson (1990) whom argued in favor of biological loss terms, i.e. grazing or sedimentation. Unfortunately no good information was given on the plankton community. However in the same study a

fourth experiment in far offshore waters provided some convincing evidence of the sought after Fe limitation (Martin *et al.*, 1990a). In offshore Antarctic waters the Fe levels may well be very low (e.g. Drake Passage, Martin *et al.*, 1990b) and limiting. Studies in offshore waters are scheduled by our group for late 1992.

Even when assuming that all nutrients in Antarctic surface waters can be converted to organic matter (e.g. by Fe fertilization), the predicted drawdown of CO_2 is modest (Peng and Broecker, 1991; Joos *et al.*, 1991). As soon as the action, e.g. fertilization with Fe, would be abandoned, the extra CO_2 taken up would rapidly be released again into the atmosphere. At a special symposium in February 1991 all evidence was presented (Chisholm and Morel, 1991) and discussed with the conclusion that intentional Fe fertilization would not likely have an effect, i.e.not to be pursued any longer (ASLO, 1991). On the other hand the role of Fe as one of several factors affecting marine productivity was clearly recognized.

DISPOSAL OF CO2 IN THE DEEP OCEAN

The various technical reports have been reviewed elsewhere (Marland, 1986; De Baar and Stoll, 1989; De Baar, 1990, 1992). Briefly one remarkable first publication (Marchetti, 1977) led to one published feasibility study (Baes *et al.*, 1980) where several options had been suggested:

a. High density solution in seawater; the reject stream would sink to the ocean floor.
b. Pure, liquefied CO_2 emitted at depths greater than 3000m for negative buoyancy.
c. Dumping solidified blocks of CO_2-hydrate at depths below 500m as to avoid bubbling.
d. Dumping solidified CO_2 (dry ice), at depths below 500m as to avoid bubbling.

For a power plant at the sea surface it is possible in principle to produce any of the above four states. The energy requirements for pressurization are not the issue here, although they would be quite significant, in the order of 30% of the energy produced when assuming a pressure of 33 atm is adequate, i.e. disposal at about 330m depth. Unfortunately the publication is very brief (and occasionally inconsistent) on the chemical stability of the material during its downfall as well as when residing at the seafloor.

Solubility of CO_2 in seawater

The partial pressure or vapor pressure of a given gas is one of the master variables. For example in our atmosphere the partial pressure of CO_2 is only about 360 x10^{-6} atm at a total pressure of 1 atm. Only in the case of a pure gas is its vapor pressure (fugacity) the same as the total pressure. The distinction between vapor and total pressure appears obvious but it has sometimes been confused. For equilibrium of CO_2 between two phases α and β the chemical potentials in both phases ought to be equal

$$\mu^{\alpha}_{CO2} = \mu^{\beta}_{CO2}$$

This can be written out as:

$$\mu^{\alpha,0}{}_{CO2} + RT \ln a^{\alpha}_{CO2} = \mu^{\beta,0}{}_{CO2} + RT \ln a^{\beta}_{CO2}$$

where a_{CO2} is the activity of CO_2 in the given phase and $\mu^{\alpha,0}{}_{CO2}$ and $\mu^{\beta,0}{}_{CO2}$ are the standard chemical potentials of CO_2 in both phases. The first problem is to assess latter parameters for each phase. Next some assessment of the activity a is required. In general the activity of a gas equals its fugacity and under ideal conditions both are also the same as its partial pressure. Under non-ideal conditions, notably at high overall pressures or deviating temperatures, this is no longer true and one defines an activity coefficient to relate partial pressure with activity.

The assumed standard temperature, salinity and depth of the deep ocean site are 2°C, S=35 at 4000m depth and represent median values (Mc Lellan, 1974). The solubility of CO_2 is a function of temperature and salinity (Weiss, 1974) at 1 atm ambient (i.e. total) pressure. At (T=2°C, S=35, p=1atm) this solubility or Henry's law constant k is 0.05822 mol.kg^{-1}.atm^{-1}. For an atmospheric partial pressure of 360 x10^{-6} atm this leads to the dissolved $(CO_2)_{aqeous}$ being 20.96 µmol.kg^{-1} in the surface water. This is furthermore in equilibrium with major dissolved forms, namely bicarbonate (HCO_3^- at about 1800-2200 µmol.kg^{-1}) and carbonate (CO_3^{2-} at about 50-200 µmol.kg^{-1}) as well as a negligible amount of H_2CO_3 (~0.02 µmol.kg^{-1}). The sum of concentrations of these various forms of CO_2 is known as ΣCO_2:

$$\Sigma CO_2 = [CO_2]_{aqeous} + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$$

The equilibria between these various forms are governed by equilibrium constants which in themselves are functions of ambient temperature and pressure. For simplicity it is assumed the deep water at the disposal site reflects equilibrium with todays atmosphere and contains above $[CO_2]_{aq.}$ at 20.96 µmol.kg^{-1}. Latter value applies to surface conditions (1 atm). Readjustment to the ambient pressure of 400 atm does not affect

ΣCO_2 but will slightly shift the equilibria such that $[CO_2]_{aq.}$ decreases to an in situ concentration of ~20 $\mu mol.kg^{-1}$ (T=2°C, S=35, p=400 atm).

Disequilibrium versus ambient seawater in the deep ocean.

a. High density solution in seawater. Seawater is equilibrated with pressurized (33 atm) pure CO_2-gas (Baes *et al.*, 1980). The activity coefficient of CO_2 is about 0.75 (2°C, 33 atm) and and its activity becomes 0.75 x 33=~25 atm. Next the above solubility of 0.05822 $mol.kg^{-1}.atm^{-1}$ at standard conditions (T=2°C, S=35, p=1atm) needs adjustment to conditions with a total pressure of 33 atm. At higher ambient pressure the solubility of CO_2 increases (Millero, 1983). For P=33 atm the solubility is 0.062 $mol.kg^{-1}.atm^{-1}$ (T=2°C, S=35, p=33 atm). The dissolved concentration then would be $[CO_2]_{aq.}$=~1.5 $mol.kg^{-1}$ similar to values shown by Baes *et al.* (1980). The amount of CO2 dissolved in the seawater will be three orders of magnitude more than the original ΣCO_2 and five orders of magnitude above the original dissolved $[CO_2]_{aq.}$When bringing this water down to 4000m depth the solubility would increase to 0.1048 mol.kg-1atm-1 at (T=2°C, S=35, p=400 atm). As such the dissolved $[CO_2]_{aq.}$=~1.5 mol.kg-1 would not have the tendency to escape. However the surrounding untreated seawater would have exactly the same solubility (0.1048 mol.kg-1atm-1) but contains only $[CO_2]_{aq.}$=~20 $\mu M.kg^{-1}$. The concentration gradient of five orders of magnitude will drive the disposed CO_2 into surrounding oceanic waters.

Baes *et al.* (1980) seemingly equate the partial pressure of CO_2 with the hydrostatic pressure, i.e. "the minimum depth of injection without bubble formation". Obviously *within* the waste stream itself there would indeed be no tendency for CO_2 bubbles to escape. However this should not be interpreted as the waste stream being chemically stable. Even if bubbles would form there would be immediate dissolution in the surrounding seawater which contains only $[CO_2]_{aq.}$=~21 $\mu mol.kg^{-1}$. At any depth (whether above or below the suggested depth level) the injected $[CO_2]_{aq.}$ will tend to diffuse into the surrounding waters.

b. Pure liquefied CO_2. Negative buoyancy of the liquid CO_2 stream can be achieved at a temperature between 0°C and 10 °C and vapor pressures greater than 300 atm, i.e. injection at depths greater than 3000m (Baes *et al.*, 1980). Chemical stability should properly be assessed from comparison of chemical potential versus that of ambient seawater (T=2°C, S=35, p=400atm). Here the activity of CO_2 in both the seawater and the pure liquefied CO_2 is important. Given the concentration $[CO_2]_{aq.}$=~20$\mu mol.kg^{-1}$ in ambient seawater and an activity coefficient of ~1.23 (Markham and Kobe, 1941) the activity would be $(CO_2)_{aq.}$=~25 $\mu mol.kg^{-1}$. In general the activity of a pure liquid is taken as unity at standard pressure (1 atm). The effect of pressure (400 atm) needs assessment by proponents of this scheme, but the activity of the pure liquid CO_2 likely will be orders of magnitude higher than in ambient seawater. More simple it might be stated that the partial or vapor presssure versus the liquid CO_2 would be 300 atm as compared to 360 x 10^{-6} atm in the ambient seawater. Hence the effluent stream would likely be grossly oversaturated versus ambient seawater, i.e. the liquefied CO_2 would in essence be unstable and dissolve into the seawater, where (under proper conditions) the below hydrates may act as transient intermediates (Sakai *et al.*, 1990).

c. Solid CO_2-hydrate. The CO_2-hydrate consists of a cubic unit cell of 46 water molecules forming 8 cages into which the CO_2 can fit, also known as a clathrate structure. The atmosphere of Mars consists for about 95 % of CO_2 with a partial pressure of 6.5 x 10^{-3} atm. and the low temperatures (~-120°C) at the Martian ice cap would be suitable for the existence of CO_2-hydrates in the ice (Miller and Smythe, 1970). The upper critical decomposition temperature was cited to be 10.2°C at a pressure of 44.5 atm above which CO_2-hydrate is unstable relative to liquid CO_2 and H_2O (Herreilers, 1936; Larson, 1955). This relates to CO_2-hydrate versus a system of *pure* CO2 and (sea)water, for example as observed at submarine gas vents (Sakai *et al.*, 1990). Apparently this led Baes *et al.* (1980) to suggest that at hydrostatic pressures greater than ~50 atm (depths > 500m) and temperature less than 12°C no more gas bubbles would form from the decomposition of the CO_2-hydrate. As with above option (a) this may not be incorrect, however this should not be interpreted as the CO_2-hydrate being stable. On the contrary the *partial* pressure of CO_2 in the ambient seawater would still be only about 360x10^{-6} atm, i.e. five orders of magnitude below the ~44.5 atm partial pressure of CO_2 as required for the CO_2-hydrate to be stable. Again this should be properly calculated through comparison of chemical potentials, where the activity of CO_2-hydrate is likely in the order of unity. Presumably both during settling as well as on the seafloor the CO_2-hydrate would tend to decompose into the surrounding seawater, as recognized by Baes et al. (1980). Similarly those submarine formations of CO_2-hydrate in direct contact with overlying seawater should be seen as transient rather then permanent features (Sakai *et al.*, 1990).

Some inconsistency about partial pressure and total pressure is apparent when reading the option of storing CO_2-hydrate at the South Pole. Here it was suggested that "the decomposition pressure of CO_2-hydrate does not fall below one atmosphere until it is cooled to about -54°C" according to (Baes *et al.*, 1980). This is consistent with the findings of Miller and Smythe (1970) for CO_2-hydrate versus the *partial* pressure of CO_2 being 1 atm at -54°C (219°K). However for the surface of the earth the partial pressure of CO_2 is only 360 x10^{-6} atm at a *total* pressure of 1 atm.

d. Solid CO_2 (dry ice). Given the activity $(CO_2)aq.=\sim 24\mu mol.kg^{-1}$ in ambient seawater it is obvious that the activity in the pure solid CO_2 is orders of magnitude higher. At standard pressure (1 atm) the activity of solid CO_2 would be near unity, the exact value at 400 atm needs assessment. However the vapor pressures for stability of dry ice are hundreds of atmospheres and would suggest the effluent stream to be grossly oversaturated versus ambient seawater. Also the temperature of dry ice is about -80°C or lower. The solidified CO_2 would be unstable as it tends to dissolve into the seawater by diffusion of both CO_2 and heat. As a matter of fact the likely reactivity with seawater has been recognized by Baes *et al.* (1980) mentioning possible reaction intermediates as CO_2-hydrate or CO_2-rich solution.

Vertical stratification.

Summarizing it is not impossible, when disregarding the expenditure, to produce any of the four physical states by selecting appropriate temperatures and pressures. This is feasible at a platform at the sea surface but also applies to natural CO_2 emissions from ocean floor vents (Sakai *et al.*, 1990). However all four physical states are (a) or appear (b,c,d) very unstable with respect to chemical dissolution in ambient seawater. The rate of dissolution depends on the rate of turbulent mixing between the disposal and the deep ocean waters. The turbulence occurring during downward transport of the plume has been studied (Baes *et al.*, 1980) and is the focus also of ongoing research (Herzog *et al.*, 1991; Zemba *et al.*, 1992). Upon arrival at the seafloor the stockpile of CO_2 in any form would remain there due to this higher density, however at its interface with overlying waters erosion would occur continuously. The rate of erosion is controlled by turbulence caused by shear stress with the lateral flow of deep ocean currents. For normal ocean basins the disposed CO_2 can therefore be modeled along with the regular deep water renewal and eventually the CO_2 would return to the atmosphere (Hoffert *et al.*, 1979). Depending on the disposal site the injected CO_2 would re-equilibrate with the atmosphere after periods in the order of ~50-500 years.

Basins with restricted deep circulation might be preferable as storage sites. For example the Deep Black Sea is stagnant (Murray *et al.*, 1991), where the inflowing high salinity Mediterranean water over the shallow Bosporus sill may not be unsuitable for CO_2 injection. Currently most of this inflowing Mediterranean water mixes with low salinity subsurface waters and flows out again at the surface of the Bosporus, yet part of it might, at least in principle, be diverted directly into the deep (>2000m) Black Sea. However in Black Sea bottom waters there is strong evidence for deep convection driven by geothermal heating (Öszoy *et al.*, 1991), i.e. considerable vertical mixing (Brunt-Vaisala frequencies < 0.01 h^{-2}; Murray *et al.*, 1991).

CALCITE DISSOLUTION

At higher total CO_2 content (ΣCO_2) seawater in general shows a lower concentration $[CO_3^{2-}]$ of the carbonate ion. As a result the deep and bottom waters of the ocean basins are undersaturated versus crystalline calcite and below the Calciumcarbonate Compensation Depth (CCD) the seafloor is devoid of calcareous sediments. Uptake of fossil fuel CO_2 in the ocean will enhance dissolution of calcite, i.e. the CCD horizon would shoal. The overall reaction may be written as

$$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2\,HCO_3^-$$

and the fossil fuel CO_2 will eventually be buffered, i.e. permanently stored. The rate of dissolution relative to the rate of fossil fuel emission is crucial. In the natural ocean the time scale of calcite dissolution is poorly known and may range from 10^3 to 10^5 years (Sundquist, 1986). At ~10^4 years (Sundquist, 1988) there will be virtually no impact towards smoothing the predicted transient peak in the atmosphere (De Baar and Stoll, 1989).

Deep ocean injection of CO2 may affect the dissolution rate and at time constants less than ~10^3 years significant buffering, i.e. permanent storage, of CO_2 may occur (Wilson, 1992). On the one hand laboratory studies of well-mixed suspensions show rate dependency on the fourth power of the decrease in $[CO_3^{2-}]$ ion concentration (Keir, 1980). On the other hand dissolution of in situ sediments is diffusion limited, where upon CO_2 disposal the (eddy) diffusion would likely diminish as bioturbation would stop once bentic fauna disappears due to the low pH of the CO_2-rich effluent. Intense vertical mixing at the benthic boundary would favor rapid buffering by calcite dissolution, this in contrast with the above search for a stratified regime (no vertical mixing) required for preserving the dense CO2-rich phases (a,b,c,d) versus overlying seawater. There is another paradox, the conservative injection model (without sediment dissolution; Hoffert *et al.*, 1979) would favor disposal at great depth, yet this generally is below the CCD horizon such that there is no $CaCO_3$ sediment to react with. Upon better understanding of the actual dissolution rate further non-conservative modeling might find disposal at intermediate depth (where existing $CaCO_3$-sediments are available for dissolution) to be favorable. With or without deep CO_2-injection, the calcite dissolution rate needs to be known more accurately for predicting the rate at which the oceans will buffer the fossil fuel CO2.

SUMMARY

Large uncertainty remains about the likelyhood of global warming, but the CO_2 increase as such already warrants implementation of curtailing measures. Reduction of fossil fuel CO_2 emissions is most imminent and will have to be achieved primarily by realistic options of both energy conservation as well as shifting to other energy sources such as biomass (De Baar, 1990; Hall *et al.*, 1991). Further research into enhancing oceanic CO_2 storage would appear justified only for developing an emergency fallback option for the future in case the realistic options have not been adequately implemented. Deep sea injection requires ~30-45% of the energy produced (DeBaar and Stoll, 1989), is applicable only to point sources representing ~30% of all fossil fuel emissions, also assuming all these plants will be relocated to the seashore. Eventually the injected CO_2 may either re-equilibrate with the atmosphere over 50-500 years, or taken up more permanently when assuming buffering by rapid dissolution of calcite sediments (Wilson, 1992).

ACKNOWLEDGEMENTS

The author is indebted to Dr. Andrew G. Dickson for advice on aspects of the thermodynamics. Dr. J. Mario J. Hoppema kindly provided comments on an earlier draft of the manuscript. Discussion with Dr. T.R.S. Wilson has led to further improvements.

REFERENCES

Anonymous (1990) Ocean iron fertilization in relation to the greenhouse effect. *U.S.JGOFS Report*, 11 (A-II),19-21.

ASLO (1991) Resolution: ocean fertilization and atmospheric carbon dioxide. In: What controls phytoplankton production in nutrient-rich areas of the open sea ? *ASLO Report*, 3-6.

Baes, C.F., Jr., S.E. Beall, D.W. Lee and G. Marland (1980) The collection, disposal and storage of carbon dioxide. In: *Interactions of energy and climate* (W. Bach, J. Pankrath and J. Williams, Eds.), Reidel, 495-519.

Banse, K. (1990) Does iron really limit phytoplankton production in the offshore subarctic Pacific ? *Limnol. Oceanogr.*, 35, 772-775.

Barnola, J.M., D.Raynaud, Y.S.Koretkovich and C.Lorius (1987) Vostok ice core provides 160,000 years record of atmospheric CO_2. *Nature*, 329, 408-414.

Berner, R.A. (1991) A model for atmospheric CO_2 over Phanerozoic time. *Amer.J.Sci.*, 291, 339-376.

Broecker, W.S. (1977) Unpublished manuscript as cited by Marland (1986).

Broecker, W.S. and G.H.Denton (1989) The role of ocean-atmosphere reorganizations in glacial cycles. *Geochim.Cosmochim.Acta*, 53, 2465-2501.

Buma, A.G.J., H.J.W. de Baar, R.F. Nolting and A.J. van Bennekom (1991) Metal enrichment experiments in the Weddell-Scotia Seas: effects of Fe and Mn on various plankton communities. *Limnol. Oceanogr.*, 36(8), 1865-1878.

Charles, C.D. and R.G.Fairbanks (1992) Evidence from Southern Ocean sediments for the effect of North Atlantic deep-water flux on climate. *Nature*, 355, 416-419.

Chisholm, S.W. and F.M.M.Morel (Eds.)(1991)What controls phytoplankton production in nutrient-rich areas of the open sea ? *Limnol. Oceanogr.*, 36(8).

Coale, K.H. (1991) The effects of iron, manganese, copper and zinc enrichments on productivity and biomass in the subarctic Pacific. *Limnol. Oceanogr.*, 36(8), 000-000.

De Baar, H.J.W. (1990) De zee: een silo voor CO_2. (The sea: a silo for CO_2). *Chemisch Magazine*, , 44, 570-574.

De Baar, H.J.W. (1992) Why not store more fossil fuel CO2 in the oceans ? Chapter 7 in: *Confining and abating CO_2 from fossil fuel burning - a feasible option ?* (E. Mot, Ed.) TNO Inst.Environm. and Energy Technol., Apeldoorn, Rept. 91-250, 71-107.

De Baar, H.J.W., A.G.J.Buma, G.Jacques, R.F.Nolting and P.J.Tréguer (1989) Trace metals iron and manganese: effects on growth. *Ber.Polarforsch.*, 65, 34-44.

De Baar, H.J.W., A.G.J.Buma, R.F.Nolting, G.C.Cadée, G.Jacques and P.J.Tréguer(1990) On iron limitation of the Southern Ocean: experimental observations in the Weddell and Scotia Seas. *Mar.Ecol. Prog.Ser.*, 65, 105-122.

De Baar, H.J.W. and M.H.C. Stoll (1989) Storage of carbon dioxide in the oceans. In: *Climate and Energy* (P.A. Okken, R.J. Swart and S. Zwerver, Eds.), Kluwer, Dordrecht, 143-177.

Goudriaan, J. (1990) Atmospheric CO_2, global carbon fluxes and the biosphere. In: R.Rabbinge et al. (eds.) *Theoretical production ecology: reflections and prospects*. PUDOC, Wageningen, 17-40.

Hall, D.O., H.E.Mynick, and R.H.Williams (1991) Cooling the greenhouse with bioenergy.*Nature*, 353, 11-12.

Herreilers, H.W. (1936) thesis, Univ. of Amsterdam.

Herzog, H., D. Golomb and S. Zemba (1991) Feasibility, modelling and economics of sequestering power plant CO_2 emissions in the deep ocean. *Environm. Progr.*, 10, 64-74.

Hoffert, M.I., Y.C. Wey, A.J.Callegari and W.S. Broecker (1979) Atmospheric response to deep-sea injections of fossil fuel carbon dioxide. *Climatic Change*, 2, 53-68.

Hoppema, J.M.J. and H.J.W. de Baar (1991) Changes in the balances of non-fossil carbon, nitrous oxide and dimethylsulfide in the NorthSea. *Neth.Inst.Sea Res. Techn.Rep.*, 1991-4, 88p.

Joos, F., J.L. Sarmiento and U. Siegenthaler(1991) estimates of the effect of Southern Ocean iron fertilization on atmospheric CO_2 concentrations. *Nature*, 349, 772-774.

Keir, R.S. (1980) The dissolution kinetics of biogenic calcium carbonates in seawater. *Geochim. Cosmochim. Acta*, 44, 241-252.

Lancelot, C., S. Mathot, C. Veth and H.J.W. de Baar (1992) On the factors controlling phytoplankton ice edge blooms in the marginal ice zone of the northwestern Weddell Sea during sea ice retreat 1988. *Polar Biol.*, submitted.

Larson, S.D. (1955) thesis, University of Illinois.

Marchetti, C. (1977) On-geo-engineering and the CO_2 problem.*Climatic Change*, 1, 59-68.

Marland, G. (1986) Technical fixes for limiting the increase of atmospheric CO_2: a review. (unpubl. manuscript).

Martin, J.H. (1990) Glacial-interglacial CO_2 change: the iron hypothesis. *Paleoceanography*, 5, 1-13.

Martin, J.H. and S. Fitzwater (1988) Iron deficiency limits phytoplankton growth in the north-east Pacific subarctic. *Nature*, 331, 341-343.

Martin, J.H., R.M. Gordon, S. Fitzwater and W.W. Broenkow (1989) Vertex: Phytoplankton/ iron studies in the Gulf of Alaska. *Deep-Sea Res.*, 36, 649-680.

Martin, J.H., R.M. Gordon and S.E. Fitzwater (1990b) Iron in Antarctic waters. *Nature*, 345, 156-158.

Martin, J.H., S.E. Fitzwater and R.M. Gordon (1990a) Iron deficiency limits phytoplankton growth in Antarctic waters. *Global Biogeochem. Cycles*, 4, 5-12.

McLellan, H.J. (1974) *Elements of physical oceanography*. Pergamon, Oxford, 16-32.

Miller, S.L. and W.D. Smythe (1970) Carbon dioxide clathrate in the Martian ice cap. *Science*, 170, 531-533.

Millero, F.J. (1983) Influence of pressure on chemical processes in the sea. Chapter 43 in: *Chemical Oceanography* (J.P. Riley and R. Chester, Eds.), 8, 2-88.

Murray, J.W., Z. Top and E.Öszoy (1991) Hydrographic properties and ventilation of the Black Sea.*Deep-Sea Res.*, 38, S663-S689.

Öszoy, E., Z.Top, G. White and J.W. Murray (1991) Double diffusive intrusions, mixing and deep sea convection in the Black Sea. In: *Black Sea Oceanography* (E.Izdar and J.W.Murray, eds.), NATO-ASI, C 351, Kluwer, Dordrecht, 17-42.

Peng, T.H. and W.S. Broecker (1991) Dynamic limitations on the Antarctic fertilization strategy. *Nature*, 349, 227-229.

Redfield, A.C., B. Ketchum and F.A. Richards(1963) The influence of organisms on the composition of seawater. Chapter in *The Sea* (M.N.Hill, ed.), 2, 26-87.

Sakai, H., T. Gamo, E.S. Kim, M. Tsutsumi, T. Tanaka, J. Ishibashi, H. Warita, M. Yamano and T. Oomori (1990) Venting of carbon dioxide-rich fluid and hydrate formation in Mid-Okinawa Trough backarc basin. *Science*, 248, 1093-1096.

Sundquist, E.T. (1986) Geological analogs: their value and limitations in carbon dioxide research. In: *The changing carbon cycle: a global analysis*. (J.R. Trabalka and D.E. Reichle, eds.), Springer, Berlin, 371-402.

Sundquist, E.T. (1988) Implications of pleistocene CO_2 changes for the long term buffering of antropogenic CO_2. Abstract in: *Eos,Trans.Am.geophys.Union*, 69, 1236.

Shackleton, N.J. and N.G. Pisias (1985) Atmospheric carbon dioxide, orbital forcing and climate. In: *The carbon cycle and atmospheric CO_2: natural variations Archean to present*. (E.T. Sundquist and W.S. Broecker, eds.) Geophys. Monogr.Ser., 32, 303-317.

Weiss, R.F. (1974) Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Mar. Chem.*, 2, 203-215.

Wilson, T.R.S. (1992) The deep ocean disposal of carbon dioxide. (this volume).

Zemba, S.G., D.S. Golomb, J.W. Dacey and A.F. Michaels (1992) Implications of deep-sea disposal of CO_2. Abstract in: *Eos, Trans.Am.geophys.Union*, 72(51), 64.